Photocycloaddition of Isocoumarins and Isothiocoumarins to Alkenes

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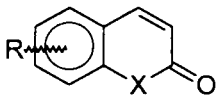
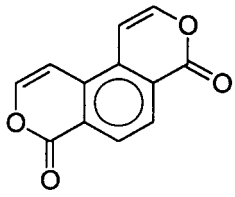
On irradiation in the presence of tetrachloroethene (TCE), both isocoumarins **3** and isothiocoumarins **4** afford in high yields the *cis*-fused cycloadducts **8** and **9**, while only the oxacycles **3** undergo photocycloaddition to 2,3-dimethylbut-2-ene (TME) to give mixtures of *cis*- and *trans*-fused products **10** and **11**, respectively, in moderate yields. This higher efficiency in reacting with TCE as compared to TME for compounds **3** and **4** contrasts the behavior of simple cyclic enones, *e.g.*, 5,5-dimethylcyclohex-2-enone (**12**), which is converted to bicyclooctanones about fifty times faster with TME than with TCE.

Introduction. – While photocycloaddition reactions of both coumarins **1** and thiocoumarins **2** to alkenes have been investigated [1–5] in some detail, reports on results of this type of reaction for the isomeric isocoumarins **3** and isothiocoumarins **4** are scarce. The parent isothiocoumarin (**4a**) is known [5] to undergo photocycloaddition to tetrachloroethene (TCE), and irradiation of the twofold isocoumarin **5** in the presence of the same alkene affords first a monocycloadduct and subsequently a mixture of biscyclobuta derivatives [6]. Here, we report results on the photocycloaddition of isocoumarins **3a**–**3c** and isothiocoumarins **4a**–**4c** to both TCE and 2,3-dimethylbut-2-ene (TME).

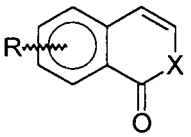


1 X = O

2 X = S



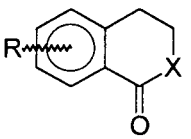
5



3 X = O

4 X = S

} **a** R = H **b** R = 5-Me **c** R = 7-Me



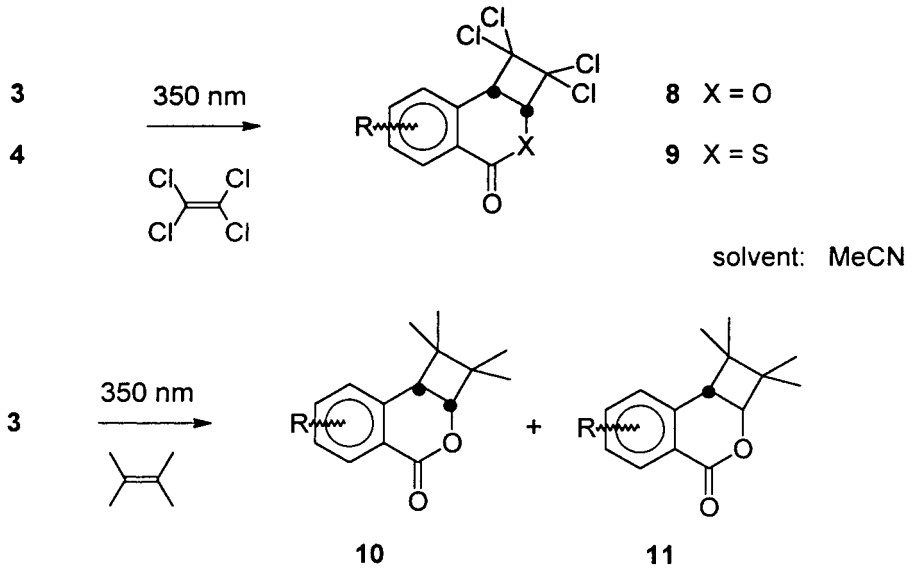
6 X = O

7 X = S

} **a** R = H **b** R = 5-Me **c** R = 7-Me

Results. – Dihydroisocoumarins **6** are convenient precursors for both isocoumarins **3** and isothiocoumarins **4**. Treatment of **6** first with the anion of α-mercaptotoluene and then with CF_3COOH [7][8] affords dihydroisothiocoumarins **7**. Compounds **6** and **7** are then converted *via* bromination/dehydrobromination sequences [8][9] to **3** and **4**, respectively. Irradiation ($\lambda = 350$ nm) of **3** or **4** in the presence of a tenfold molar excess of TCE in MeCN affords the *cis*-fused cyclobuta derivatives **8** and **9**, respectively. The structures of **9b** and **9c** were established by X-ray analysis. Rates of conversion **4** → **9** are faster, *i.e.*, the yields of isolated products are higher for the S- than the O-heterocycles. Irradiation of **3** in the presence of a tenfold molar excess of TME gives mixtures of *cis*- and *trans*-fused cyclobuta derivatives **10** and **11**, while compounds **4**, under the same conditions, do not undergo any reaction (*Scheme 1*). Rates of conversion of **3** to **8** are about twice as fast as those for the formation of **10** and **11**. In both series (**3** and **4**), the parent compounds, *i.e.*, **3a** and **4a**, react slower with both alkenes by a factor of 5 than the corresponding methyl derivatives.

Scheme 1



Irradiation of 5,5-dimethylcyclohex-2-enone (**12**) in the presence of TCE affords the *cis*-fused bicyclo[4.2.0]octanone **13**, and irradiation in the presence of TME a 1:3 mixture of *cis*- and *trans*-fused bicyclo[4.2.0]octanones **14** and **15** (*Scheme 2*). In contrast to the results with compounds **3** and **4**, enone **12** reacts *ca.* 50 times faster with TME than with TCE. The relative rates of conversion for these different precursors in the [2 + 2] photocycloadditions are summarized in the *Table*.

Finally, we recorded cyclic voltammogramms for the reduction of **3a** and **4a**. The reduction on Hg of both compounds (DMF, Bu_4NBr) proceeds by a reversible one-electron transfer. The peak potentials at scan rate of 200 $mV \cdot sec^{-1}$ for **3a** are $Ep_c = -1.52$ V and $Ep_a = 1.46$ V, and for **4a** $Ep_c = -1.31$ V and $Ep_a = -1.25$ V.

Scheme 2

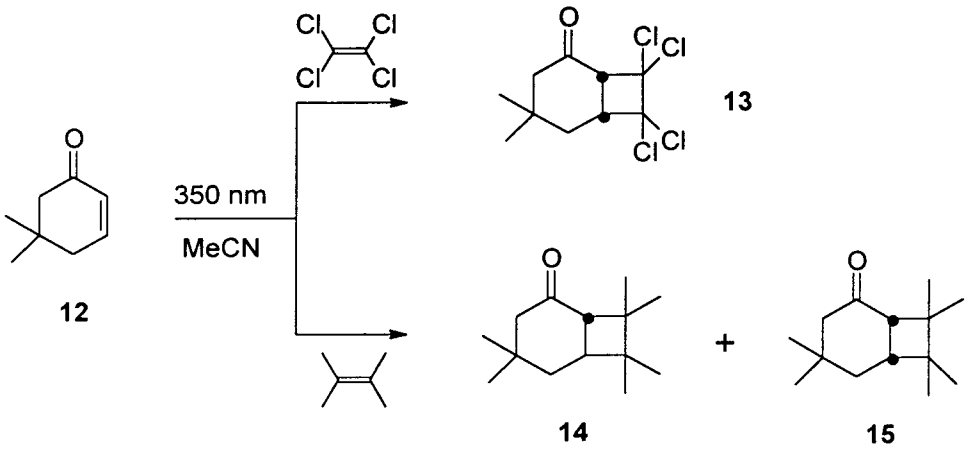


Table. *Relative Rates for Conversion to Products on Irradiation of Compounds* **3**[a]), **4**[b]), *and* **12** *in the Presence of Either TCE or TME*

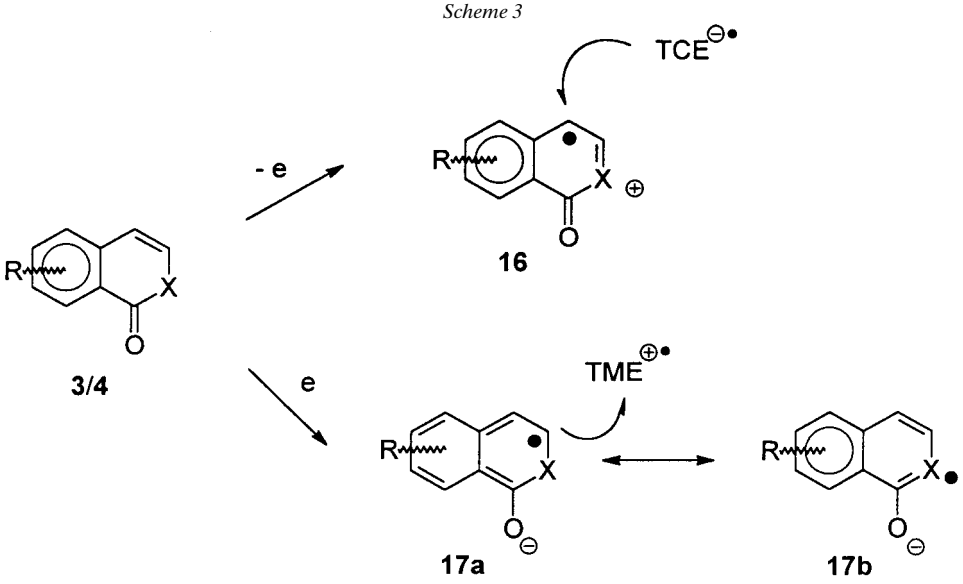
	12	**3**	**4**
Alkene			
TCE	20	2	5
TME	1000	1	$\ll 1$

[a]) Average value for **3a**, **3b**, and **3c**.
[b]) Average value for **4a**, **4b**, and **4c**.

Discussion. – The most striking aspect in the results presented above seems to be the finding that excited compounds **3** and **4** react more efficiently with TCE than with TME, while, for cyclohexenones, *e.g.*, **12**, cyclobuta-annelation occurs in reverse order with the same alkenes. Indeed, already early competition experiments had shown [10–12] that the rates of reaction of cyclic enones with several alkenes decrease with decreasing alkene electron density, albeit TCE has never been used in such studies. It is, therefore, reasonable to assume that the selectivity observed for the excited 'styrenic' C=C bond in **3** and **4** is due to the formation of triplet exciplexes with (opposed) partial charge-transfer character [13] for each alkene, *i.e.*, TCE ($IP = 9.32$ eV) is partially reduced and TME ($IP = 8.30$ eV) partially oxidized, respectively. Radical-ion structures **16** on the one side, and **17a** and **17b** on the other side, should represent good descriptions for such intermediates in the reactions of **3** or **4**, and, from these, one can expect bonding from **16** to TCE to occur at the benzylic position and bonding from resonance structure **17a** to TME to occur on the C-atom adjacent to the heteroatom (*Scheme 3*).

This concept also helps to explain the finding that isothiocoumarins **4**, in contrast to isocoumarins **3**, do not undergo photocycloaddition to TME. On the one side, the contribution of resonance structure **17b** for the S-heterocycles becomes much more important than for the benzopyrans, a fact illustrated by the formation of a reasonably

Scheme 3



stable 9-phenylthioxanthyl radical in the one-electron reduction of 9-phenylthioxanthylium perchlorate [14], and, therefore, bonding of an alkene to **17a** should be much more favorable for the O-heterocycles. On the other side, estimation of the electron accepting abilities, *i.e.*, the term $(E^{red} + E_{0,0})$ for excited **3** and **4** gives values of $(-1.49 + 3.72) = 2.23$ eV for **3a** and of $(-1.28 + 3.30) = 2.02$ eV for **4a**, which suggests that (partial) charge transfer to excited isocoumarins occurs easier than to excited isothiocoumarins. Thus, both these interpretations corroborate the reactivities of **3** and **4** in photocycloadditions to alkenes.

Finally, for both types of heterocycles the Me-substituted derivatives react with TCE as well as with TME much more efficiently than the parent (unsubstituted) compounds **3a** and **4a**. Photophysical studies with various isocoumarins and isothiocoumarins are now in progress in order to clarify these findings.

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Experimental Part

1. *General.* Photolyses: *Rayonet RPR-100* photoreactor equipped with 350-nm lamps. Anal. GC: 30-m *SE 30* capillary column. Prep. GC: 2-m 5% *SE 30* on *Chromosorb W-AW*. UV Spectra: in MeCN, in nm (log ε). ^{1}H- and ^{13}C-NMR Spectra: in $CDCl_3$ at 500 and 125.8 MHz, resp.; chemical shifts in ppm rel. to TMS (=0 ppm). MS: at 70 eV; in *m*/*z* (rel. intensity in %). X-Ray analyses were run on an *Enraf-Nonius CAD-4* four-circle diffractometer at 293 K with CuK_α radiation ($\lambda = 1.54178$ Å). Cyclic voltammetry: a potentiostat and electronic ramp generator (*Metrohm E612*), a potentiometric *XY* recorder and a Pt anode (counter electrode), a hanging Hg drop (working electrode), and Ag/AgBr (reference electrode) were used.

2. *Starting Materials.* Isocoumarins **3a** [15], **3b** [16], and **3c** [8], isothiocoumarins **4a** [15] and **4c** [8], and *5,5-dimethylcyclohex-2-enone* (**12**) [17] were synthesized according to the literature procedures.

2.1. *Synthesis of* **4b**. Ring opening of *3,4-dihydro-5-methyl-1*H*-2-benzopyran-1-one* (**6b**) [9] with α-mercaptotoluene and subsequent treatment of the resulting crude 2-[2-(benzylthio)ethyl]benzoic acid with

CF_3COOH according to [7][8] afforded *5-methyl-3,4-dihydro-1*H*-2-benzothiopyran-1-one* (**7b**). Yield 20%. M.p. 58°. UV: 300 (3.242), 270 (3.823). ^{1}H-NMR: 7.83 (*d*, *J* = 7.6); 7.37 (*d*, *J* = 7.6); 7.25 (*t*, *J* = 7.6); 3.24, 3.17 (*AA′BB′*, 4 H); 2.36 (*s*, 3 H). ^{13}C-NMR: 191.6 (*s*); 139.5 (*s*); 135.8 (*s*); 135.1 (*d*); 132.6 (*s*); 126.6 (*d*); 124.8 (*d*); 27.9 (*t*); 25.8 (*t*); 20.1 (*q*). MS: 178 (95, $M^{+\bullet}$), *150*.

Bromination and dehydrobromination of **7b** according to [8] afforded *5-methyl-1*H*-2-benzothiopyran-1-one* (**4b**). Yield 65%. M.p. 96°. UV: 361 (3.423), 346 (3.624), 299 (3.741), 287 (3.792), 272 (3.912), 247 (4.313), 241 (4.322). ^{1}H-NMR: 8.17 (*d*, *J* = 8.2); 7.57 (*d*, *J* = 7.7); 7.43 (*dd*, *J* = 7.7, 8.2); 7.38 (*d*, *J* = 10.2); 7.14 (*d*, *J* = 10.2); 2.45 (*s*, 3 H). ^{13}C-NMR: 186.8 (*s*); 136.3 (*s*); 135.3 (*d*); 129.3 (*s*); 128.3 (*d*); 124.9 (*s*); 124.8 (*d*); 123.9 (*d*); 117.9 (*d*); 20.1 (*q*). MS: *176* ($M^{+\bullet}$).

3. *Photolyses.* Ar-Degassed solns. containing either **3**, **4**, or **12** (1 mmol) and the alkene (TCE or TME, 10 mmol) in MeCN (10 ml) were irradiated for the time and up to the degree of conversion of starting material indicated. After evaporation of the solvent, the following workup procedures were used: in the irradiations with TCE, the product was isolated/purified by chromatography (SiO_2; CH_2Cl_2) as all TCE-cycloadducts decomposed during GC analysis; and in the irradiations with TME, the products were obtained by prep. GC.

Irradiation of **3a** *in the Presence of TCE*. After 48 h monitoring by ^{1}H-NMR indicated that only 5% of starting material were converted to a product with cyclobutane H-atoms at 5.52 and 4.61 ppm, *J* = 7.9 Hz, most probably **8a**, isolation of which failed.

Irradiation of **3b** *in the Presence of TCE*. After 48 h from a mixture of 18% **3b** and 82% **8b**, 240 mg (74%) of *2aα,8bα-1,1,2,2-tetrachloro-2,2a-dihydro-8-methyl-1*H*-cyclobuta[*c*][2]benzopyran-4-one* (**8b**) were obtained. M.p. 122°. ^{1}H-NMR: 8.12 (*d*, *J* = 7.6); 7.55 (*d*, *J* = 7.6); 7.46 (*t*, *J* = 7.6); 5.41 (*d*, *J* = 7.9); 4.77 (*d*, *J* = 7.9); 2.50 (*s*, 3 H). ^{13}C-NMR: 161.0 (*s*); 137.6 (*s*); 136.3 (*d*); 130.6 (*s*); 129.5 (*d*); 128.6 (*d*); 124.0 (*s*); 92.8 (*s*); 91.9 (*s*); 80.3 (*d*); 47.7 (*d*); 19.8 (*q*).

Irradiation of **3c** *in the Presence of TCE*. After 48 h from a mixture of 30% **3c** and 70% **8c**, 192 mg (60%) *2aα,8bα-1,1,2,2-tetrachloro-2,2a-dihydro-6-methyl-1*H*-cyclobuta[*c*][2]benzopyran-4-one* (**8c**) were obtained. M.p. 124°. ^{1}H-NMR: 8.05 (*d*, *J* = 1.0); 7.50 (*dd*, *J* = 1.0, 7.6); 7.29 (*d*, *J* = 7.6); 5.50 (*d*, *J* = 8.1); 4.58 (*d*, *J* = 8.1); 2.44 (*s*, 3 H). ^{13}C-NMR: 160.5 (*s*); 140.2 (*s*); 135.2 (*d*); 130.9 (*d*); 129.3 (*d*); 128.9 (*s*); 123.2 (*s*); 92.8 (*s*); 91.6 (*s*); 79.8 (*d*); 49.9 (*d*); 21.3 (*q*).

Irradiation of **4a** *in the Presence of TCE*. After 12 h, a mixture of 45% **4a** and 55% **9a** [5] was obtained.

Irradiation of **4b** *in the Presence of TCE*. After 12 h (total conversion to **9b**), 330 mg (97%) *2aα,8bα-1,1,2,2-tetrachloro-2,2a-dihydro-8-methyl-1*H*-cyclobuta[*c*][2]benzothiopyran-4-one* (**9b**) were obtained. M.p. 164°. ^{1}H-NMR: 8.02 (*d*, *J* = 7.6); 7.53 (*d*, *J* = 7.6); 7.41 (*t*, *J* = 7.6); 5.07 (*d*, *J* = 10.2); 4.96 (*d*, *J* = 10.2); 2.55 (*s*, 3 H). ^{13}C-NMR: 186.9 (*s*); 138.9 (*s*); 136.3 (*d*); 131.8 (*s*); 131.1 (*s*); 128.7 (*d*); 125.2 (*d*); 95.1 (*s*); 94.0 (*s*); 53.6 (*d*); 47.7 (*d*); 20.9 (*q*).

X-Ray Crystal-Structure Determination of **9b**: Pale yellow transparent blocks (0.30 × 0.60 × 0.80 mm) from CH_2Cl_2, $C_{12}H_8Cl_4OS$, M_r 324.06, monoclinic, space group *P*21/*n*, *Z* = 4, *a* = 6.499(7), *b* = 10.052(9), *c* = 21.295(1) Å, *β* = 105.94(7)°, *V* = 1338(2) Å^3, D_x = 1.698 g/cm^{-3}.

Irradiation of **4c** *with TCE*. After 12 h (total conversion to **9c**), 320 mg (93%) *2aα,8bα-1,1,2,2-tetrachloro-2,2a-dihydro-6-methyl-1*H*-cyclobuta[*c*][2]benzothiopyran-4-one* (**9c**) were obtained. M.p. 128°. ^{1}H-NMR: 7.95 (*d*, *J* = 1.5); 7.47 (*dd*, *J* = 1.5, 7.6); 7.27 (*d*, *J* = 7.6); 4.95 (*d*, *J* = 9.7); 4.76 (*d*, *J* = 9.7); 2.43 (*s*, 3 H). ^{13}C-NMR: 186.6 (*s*); 139.8 (*s*); 134.8 (*d*); 130.7 (*d*); 130.0 (*s*); 129.5 (*s*); 127.4 (*d*); 94.6 (*s*); 93.9 (*s*); 53.7 (*d*); 49.9 (*d*); 21.2 (*q*).

X-Ray Crystal-Structure Determination of **9c**. Pale yellow transparent blocks (0.20 × 0.60 × 0.70 mm) from CH_2Cl_2, $C_{12}H_8Cl_4OS$, M_r 324.06, triclinic, space group *P*1, *Z* = 2, *a* = 6.471(7), *b* = 9.686(9), *c* = 11.815(9) Å, *α* = 79.46(7)°, *β* = 77.38(7)°, *γ* = 73.28(8)°, *V* = 686.4(1) Å^3, D_x = 1.655 g/cm^{-3}.

Irradiation of **12** *in the Presence of TCE*. After 24 h from a mixture of 33% **12** and 67% **13**, 150 mg (52%) *1α,6α-7,7,8,8-tetrachloro-4,4-dimethylbicyclo[4.2.0]octan-2-one* (**13**) were obtained. M.p. 56–58°. ^{1}H-NMR: 3.77 (*d*, *J* = 9.5); 3.44 (*ddd*, *J* = 8.5, 9.5, 12.3); 2.37 (*d*, *J* = 17.5); 2.27 (*dd*, *J* = 0.5, 17.5); 2.03 (*dd*, *J* = 12.3, 13.5); 1.53 (*ddd*, *J* = 0.5, 8.5, 13.5); 1.10 (*s*, 3 H); 0.87 (*s*, 3 H). ^{13}C-NMR: 201.1 (*s*); 92.8 (*s*); 90.2 (*s*); 54.4 (*d*); 52.9 (*t*); 50.1 (*d*); 36.2 (*t*); 32.0 (*s*); 30.5 (*q*); 25.4 (*q*). MS: 290 (0.5, $M^{+\bullet}$), *150*.

Irradiation of **3a** *in the Presence of TME*. After 96 h, a mixture of 79% **3a**, 18% **10a**, and 3% **11a** was obtained as monitored by GC. ^{1}H-NMR (from the mixture): cyclobutane H-atoms at 4.80 and 3.47 ppm, *J* = 7.6 for **10a**, and 4.14 and 3.24 ppm, *J* = 12.2 for **11a**.

Irradiation of **3b** *in the Presence of TME*. After 96 h, from a mixture of 30% **3b**, 58% **10b**, and 12% **11b**, pure *2aα,8bα-2,2a-dihydro-1,1,2,2,8-pentamethyl-1*H*-cyclobuta[*c*][2]benzopyran-4-one* (**10b**) was obtained by prep. GC (190°) as first fraction. M.p. 69°. ^{1}H-NMR: 8.07 (*d*, *J* = 7.9); 7.39 (*d*, *J* = 7.9); 7.27 (*t*, *J* = 7.9); 4.70 (*d*, *J* = 7.4); 3.62 (*d*, *J* = 7.4); 2.26 (*s*, 3 H); 1.24 (*s*, 6 H); 1.06 (*s*, 3 H); 0.79 (*s*, 3 H). ^{13}C-NMR: 163.2 (*s*); 137.4 (*s*);

136.6 (*s*); 135.6 (*d*); 128.5 (*d*); 127.3 (*d*); 124.4 (*s*); 81.8 (*d*); 44.8 (*s*); 44.4 (*s*); 40.2 (*d*); 26.5, 24.5, 22.3, 19.9, 17.5 (5*q*). MS: 244 (20, $M^{+\cdot}$), *161*.

The second fraction consisted of 75% *2aα,8bβ-2,2a-dihydro-1,1,2,2,8-pentamethyl-1*H-*cyclobuta*[c]*[2]benzopyran-4-one* (**11b**) contaminated with 25% of **10b**. ^{1}H-NMR: 7.94 (*d*, *J* = 7.9); 7.37 (*d*, *J* = 7.9); 7.24 (*t*, *J* = 7.9); 4.18 (*d*, *J* = 12.0); 3.24 (*d*, *J* = 12.0); 2.33 (*s*, 3 H); 1.29 (*s*, 3 H); 1.28 (*s*, 3 H); 1.17 (*s*, 3 H); 1.10 (*s*, 3 H). ^{13}C-NMR: 167.2 (*s*); 137.6 (*s*); 136.3 (*s*); 130.4 (*d*); 127.9 (*d*); 126.9 (*d*); 126.5 (*s*); 81.6 (*d*); 47.0 (*s*); 46.5 (*d*); 42.0 (*s*); 24.8, 22.8, 20.9, 19.8, 18.3 (5*q*). MS: 244 (5, $M^{+\cdot}$), *173*.

Irradiation of **3c** *in the Presence of TME*. After 96 h, from a mixture of 32% **3c**, 61% **10c**, and 7% **11c**, pure *2aα,8bα-2,2a-dihydro-1,1,2,2,6-pentamethyl-1*H-*cyclobuta*[c]*[2]benzopyran-4-one* (**10c**) was obtained first by prep. GC (190°). M.p. 62°. ^{1}H-NMR: 8.00 (*s*); 7.33 (*d*, *J* = 7.6); 6.95 (*d*, *J* = 7.6); 4.78 (*d*, *J* = 7.6); 3.42 (*d*, *J* = 7.6); 2.37 (*s*, 3 H); 1.18 (*s*, 3 H); 1.17 (*s*, 3 H); 0.99 (*s*, 3 H), 0.76 (*s*, 3 H). ^{13}C-NMR: 165.4 (*s*); 137.1 (*s*); 134.5 (*d*); 134.4 (*s*); 130.5 (*d*); 128.4 (*d*); 123.9 (*s*); 80.9 (*d*); 44.7 (*s*); 42.8 (*s*); 41.6 (*d*); 26.2, 23.9, 21.4, 21.3, 18.1 (5*q*). MS: 244 (5, $M^{+\cdot}$), *161*.

The second fraction consisted of 55% *2aα,8bβ-2,2a-dihydro-1,1,2,2,6-pentamethyl-1*H-*cyclobuta*[c]*[2]benzopyran-4-one* (**11c**) contaminated with 45% of **10c**. ^{1}H-NMR: 7.81 (*s*); 7.15 (*d*, *J* = 7.6); 6.71 (*d*, *J* = 7.6); 4.08 (*d*, *J* = 12.2); 3.19 (*d*, *J* = 12.2); 2.39 (*s*, 3 H); 1.28 (*s*, 3 H); 1.22 (*s*, 3 H); 1.15 (*s*, 3 H), 1.09 (*s*, 3 H). ^{13}C-NMR: 161.0 (*s*); 138.8 (*s*); 134.0 (*d*); 131.0 (*s*); 130.8 (*d*); 128.0 (*d*); 123.3 (*s*); 81.8 (*d*); 46.9 (*s*); 45.5 (*d*); 41.9 (*s*); 24.8, 22.4, 21.4, 19.9, 17.7 (5*q*). MS: 244 (6, $M^{+\cdot}$), *173*.

Irradiation of **12** *in the Presence of TME*. After 4 h (total conversion to products), a 3 : 1 mixture **14**/**15** was obtained. Separation by prep. GC (150°) afforded first *1α,6β-4,4,7,7,8,8-hexamethylbicyclo[4.2.0]octan-2-one* (**14**). Colorless liquid. ^{1}H-NMR: 2.36 (*d*, *J* = 13.3); 2.25 (*ddd*, *J* = 3.8, 12.0, 13.3); 2.13 (*d*, *J* = 13.6); 1.87 (*dd*, *J* = 1.0, 13.6); 1.47 (*dd*, *J* = 12.0, 12.3); 1.41 (*ddd*, *J* = 1.0, 3.8, 12.3); 1.21 (*s*, 3 H); 1.07 (*s*, 3 H); 1.02 (*s*, 3 H); 1.01 (*s*, 3 H); 0.91 (*s*, 3 H); 0.90 (*s*, 3 H). ^{13}C-NMR: 208.1 (*s*); 56.3 (*d*); 55.6 (*t*); 47.6 (*d*); 42.9 (*s*); 42.3 (*s*); 40.1 (*s*); 39.3 (*t*); 32.7, 28.2, 23.6, 22.9, 19.3, 18.3 (6*q*). MS: 208 (2.5, $M^{+\cdot}$), *110*.

The second fraction consisted of 85% *1α,6α-4,4,7,7,8,8-hexamethylbicyclo[4.2.0]octan-2-one* (**15**) contaminated with 15% of **14**. ^{1}H-NMR: 2.70 (*d*, *J* = 8.9); 2.18 (*ddd*, *J* = 8.5, 8.9, 12.6); 2.16 (*d*, *J* = 17.7); 1.97 (*dd*, *J* = 2.8, 17.7); 1.68 (*dd*, *J* = 12.6, 13.2); 1.58 (*ddd*, *J* = 2.8, 8.5, 13.2); 1.14 (*s*, 3 H); 1.04 (*s*, 3 H); 1.03 (*s*, 3 H); 1.02 (*s*, 3 H); 0.92 (*s*, 3 H); 0.82 (*s*, 3 H). ^{13}C-NMR: 214.4 (*s*); 54.9 (*t*); 49.2 (*d*); 43.6 (*s*); 39.4 (*d*); 38.6 (*s*); 36.7 (*t*); 32.7 (*s*); 32.0 (*s*); 31.5, 27.7, 26.0, 25.8, 23.2, 18.7 (6*q*). MS: 290 (0.5, $M^{+\cdot}$), *110*.

Comparative Irradiations of **3, 4**, *and* **12** *in the Presence of Alkenes.* Ar-Degassed solns., which contain 0.30 mmol of alkene and 0.015 mmol of either **3**, **4**, or **12** in 1 ml of MeCN, were irradiated in a merry-go-round setup, and the formation of products was monitored by GC.

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